

Synthesis of **4**: A dry, argon-flushed Schlenk tube was charged with phenylhydrazine **3** (1.0 equiv) in absolute dichloromethane (10 mL mmol⁻¹) and with tetrafluoroboric acid (1 equiv) in absolute diethyl ether (54 wt %). The solution was stirred for 30 minutes at room temperature, and then evaporated under reduced pressure. The highly hygroscopic salt was dissolved in orthoformate:methanol (2:1, 20 equiv) and transferred under argon into a pyrex tube; the sealed tube was then heated in a sand bath at 80 °C for 12 h. The mixture was cooled to room temperature and concentrated in vacuo. The crude product was dried under high vacuum for 2 h. The residue was recrystallized from methanol to give the triazolium salt **4** as an ochre crystalline solid in 65 % yield.

Synthesis of **6** (general procedure): The aromatic aldehyde (10 mmol) was added to a solution of **4** (331 mg, 1 mmol, 10 mol %) in absolute THF (0.7 mL mmol⁻¹) at room temperature. The reaction mixture was tempered for 5 min, then KOtBu (112 mg, 1 mmol, 10 mol %) in absolute THF (0.4 mL mmol⁻¹) was added dropwise. The reaction mixture was stirred for 16 h, poured into water, extracted twice with dichloromethane, and dried (MgSO₄). The solvent was evaporated and the residue was purified by column chromatography (silica gel, diethyl ether:pentane 1:1) or by crystallization to give the aromatic acyloins as colorless crystalline solids or pale yellow oils.

Received: December 5, 2001 [Z18335]

New Catalyst Systems for the Catalytic Conversion of Methane into Methanol**

Michael Muehlhofer, Thomas Strassner,* and Wolfgang A. Herrmann

The catalytic conversion of methane into methanol is one of the major challenges for chemists. Methane, as the major part of natural gas, is currently the cheapest source for hydrocarbons, and the need for methanol will increase in the near future. Catalytic homogeneous oxidation at low temperatures is economically interesting, but also very difficult to achieve as a result of the high stability of C–H bonds. Metal centers which allow a direct oxidative addition are probably needed for this approach to succeed.

Palladium and platinum compounds have been successfully used for the functionalization of alkanes and arenes.^[1, 2] After the pioneering work of Shilov and Shteinman,^[3] Periana et al.^[2] and Fujiwara et al.,^[1] in particular, reported interesting results. Some of the ligands which have been used in C–H activation are shown in Figure 1.

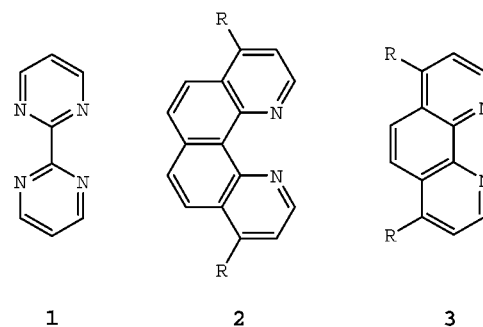


Figure 1. Ligands which have been successfully used in C–H activation reactions.

Up to now the catalytic system described by Periana and co-workers, a platinum complex with the bipyrimidine ligand **1**, has proven to be the most efficient and highly selective system providing methanol in yields of up to 72 %.^[4] The major drawback of the system is the reaction medium: oleum leads to a large amount of diluted sulfuric acid when the formed ester is hydrolyzed. Very recently an even higher activity was reported for palladium and platinum complexes of ligand **3**.^[5] This structural motif can also be found in other ligands, such as **2**, which are derived from 1,10-phenanthroline (Figure 1).^[6] In general, however, only a small number of systems which are capable of functionalizing methane catalytically has been

- [1] T. Ugai, S. Tanaka, S. Dokawa, *J. Pharm. Soc. Jpn.* **1943**, 63, 269–300; [*Chem. Abstr.* **1951**, 45, 5148e].
- [2] a) R. Breslow, *J. Am. Chem. Soc.* **1958**, 80, 3719–3726; b) R. Breslow, R. Kim, *Tetrahedron Lett.* **1994**, 35, 699–702.
- [3] J. Sheehan, D. H. Hunneman, *J. Am. Chem. Soc.* **1966**, 88, 3666–3667.
- [4] J. Sheehan, T. Hara, *J. Org. Chem.* **1974**, 39, 1196–1199.
- [5] W. Tagaki, Y. Tamura, Y. Yano, *Bull. Chem. Soc. Jpn.* **1980**, 53, 478–480.
- [6] C. Zhao, S. Chen, P. Wu, Z. Wen, *Huaxue Xuebao* **1988**, 46, 784–790.
- [7] J. Marti, J. Castells, F. López-Calahorra, *Tetrahedron Lett.* **1993**, 34, 521–524.
- [8] R. L. Knight, F. J. Leeper, *Tetrahedron Lett.* **1997**, 38, 3611–3614.
- [9] A. U. Gerhard, F. J. Leeper, *Tetrahedron Lett.* **1997**, 38, 3615–3618.
- [10] C. A. Dvorak, V. H. Rawal, *Tetrahedron Lett.* **1998**, 39, 2925–2928.
- [11] a) D. Enders, K. Breuer, J. H. Teles, *Helv. Chim. Acta* **1996**, 79, 1217–1221; b) D. Enders, K. Breuer, *Comprehensive Asymmetric Catalysis*, Vol. 3, Springer, Heidelberg, **1999**, pp. 1093–1102.
- [12] R. L. Knight, F. J. Leeper, *J. Chem. Soc. Perkin. Trans. 1* **1998**, 1891–1893.
- [13] a) D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem.* **1995**, 107, 1119–1122; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 1021–1024; b) J. H. Teles, J.-P. Melder, K. Ebel, R. Schneider, E. Gehr, W. Harder, S. Brode, D. Enders, K. Breuer, G. Raabe, *Helv. Chim. Acta* **1996**, 79, 61–83.
- [14] For the synthesis from *L*-tert-leucine by reduction (a) and cyclization (b), see: a) D. A. Dickman, A. I. Meyers, G. A. Smith, R. E. Ganley, *Org. Synth.* **1990**, Coll. Vol. 7, 530–533; b) M. S. Newman, A. Kutner, *J. Am. Chem. Soc.* **1951**, 73, 4199–4204.
- [15] H. G. Rule, J. Crawford, *J. Chem. Soc.* **1937**, 138–145.

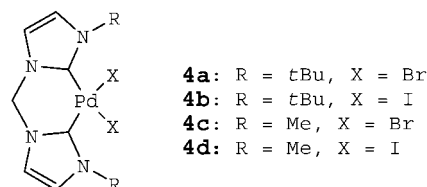
[*] Dr. T. Strassner, M. Muehlhofer, Prof. Dr. W. A. Herrmann
Technische Universität München
Anorganisch-chemisches Institut
Lichtenbergstrasse 4, 85747 Garching (Germany)
Fax: (+49) 89-289-13473
E-mail: thomas.strassner@ch.tum.de

[**] C–H activation by N-heterocyclic carbenes, Part 1. This work was supported by Süd-Chemie AG.

Supporting information for this article is available on the WWW under <http://www.angewandte.com> or from the author.

published,^[7–10] with many of them dealing with the direct carbonylation to form acetic acid.^[1, 11–16]

We now report for the first time the use of N-heterocyclic carbene (NHC) complexes for the catalytic activation of methane. We found that solutions of palladium(II) complexes of NHCs in carboxylic acids catalyze the conversion of methane into the corresponding methyl esters. High thermal stability of palladium(II)–carbene complexes was shown, for example by **4a** (Figure 2),^[17] but an extraordinary feature is

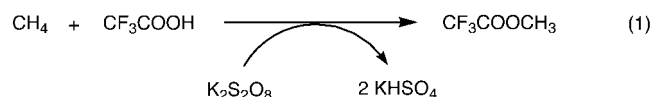


4

Figure 2. Palladium(II) complexes with chelating biscarbene ligands.

the unprecedented resistance of the NHC complexes under the acidic conditions which are necessary for C–H activation.

A suspension of potassium peroxodisulfate in a mixture of trifluoroacetic acid and trifluoroacetic acid anhydride at a methane pressure of 20–30 bar and 80–100 °C in the presence of catalytic amounts of **4** leads to the formation of trifluoroacetic acid methyl ester. Equation (1) shows the oxidative character of the reaction which formally can be described as $\text{CH}_4 \rightarrow [\text{CH}_3]^+ + \text{H}^+ + 2\text{e}^-$.



The analogous platinum complexes^[18] can not be used as catalysts, since they immediately decompose in trifluoroacetic acid to platinum black, whereas compounds **4a–4d** form clear yellow solutions in the same solvents, which do not show signs of decomposition (NMR) even after 20 hours. The characteristic pattern of the ¹H NMR signals for the bridging methylene groups does not change, thus a reprotonation of the carbene ligands to the corresponding bisimidazolium salts can be excluded. The complexes are also stable against the addition of strong oxidants and no precipitation of palladium(II) salts was observed.

Therefore palladium–NHC complexes fulfill the requirements for catalysts which are suitable for C–H activation: a strong acid can be used as the reaction medium to protect the formed alcohols against overoxidation by forming an ester;^[8] the NHC ligands stabilize the strong Lewis acidic metal centers, which can bind the methyl species formed by activation of a C–H bond in methane; and the extraordinary thermal and chemical stability allows reactions to be performed at higher temperatures in the presence of strong oxidants.

For the catalytic functionalization of methane a suspension of **4a** (0.21 mmol) and K₂S₂O₈ (100 equiv) in a mixture of

trifluoroacetic acid (60 mL) and trifluoroacetic acid anhydride (10 mL) were transferred into an autoclave. The only product formed with an initial methane pressure of 20 bar and a temperature of 80 °C was trifluoroacetic acid methyl ester. The conversion is greater than 500 % relative to palladium.

The choice of the counterion has a significant influence on the activity of the catalyst, since according to GC–MS analysis no methyl ester is produced by compound **4b**. The quantum chemically optimized structure of compound **4c** shows that the six-membered ring formed by the palladium center and the chelating biscarbene ligand has a strained boat conformation (Figure 3).^[19] Besides the negative influence of the

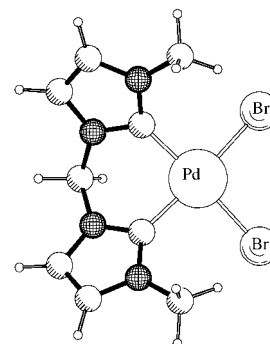


Figure 3. Pluton^[20] plot of the quantum-chemically optimized structure (B3LYP/6-31G*)^[21–24] of complex **4c**.

sterically more demanding *tert*-butyl groups of **4b**, the relatively low basicity of the iodide ligands compared to the bromide ligands enhances the difficulties in creating a free coordination site by protonation of the halogen ligands. According to this rationalization, the use of compound **4c**, where the steric demand of the ligands R (methyl) is significantly lower, approximately doubles the yield (980 % relative to palladium), while **4d** does not produce any ester at all.

Control experiments with palladium(II) acetate and similar salts show, that the NHC ligands have a significant effect on the activation (Table 1). Under these conditions the system of Sheldon and co-workers [Pd(L)(OAc)₂] (L = 4,7-diphenyl-1,10-phenanthroline disulfuric acid disodium salt),^[6] the system of Periana and co-workers [Pt(bpym)Cl₂] (bpym = bipyridinium), [Pd(phen)Cl₂] (phen = 1,10-phenanthroline), or a reaction without catalyst at all did not yield traceable

Table 1. Catalytic conversion of methane into methanol.

Entry	Catalyst	Yield ^[a] [%]
1	4a	510
2	4b	0
3	4c	980
4	4d	0
5	Pd(OAc) ₂	380
6	Sheldon system	0
7	Periana system	0
8	none	0
9	4c	3000 ^[b]

[a] By GC analysis, relative to palladium. [b] *T* = 90 °C, *t* = 14 h, *p*(CH₄) = 30 bar.

amounts of ester. Additional reactions under different conditions show that the limit of the palladium system has not yet been reached. A yield of 3000% relative to palladium (TON = 30) could be reached in 14 hours with **4c** at 90 °C and an initial methane pressure of 30 bar.

The use of trifluoroacetic acid has the additional advantage that the formed ester can easily be removed from the reaction mixture by distillation, hydrolyzed, and the recovered acid together with remaining methane can be transferred back. Therefore, it is possible to run it as a cyclic process.

In summary a new field for the application of NHC complexes has opened up with C–H activation. Up to now they have been mainly used for olefin metathesis,^[25–29] hydroformylation,^[30, 31] or C–C coupling reactions.^[32–34] The unexpected high stability in strong acids and under oxidative conditions allows the use of the compounds described here for catalytic C–H activation of methane. In view of the significantly lower bond energies of higher alkanes and arenes there is a multitude of other applications, which are currently under investigation.

Experimental Section

Catalytic oxidation of methane: Catalyst **4** (0.21 mmol) was dissolved in a mixture of trifluoroacetic acid (60 mL) and trifluoroacetic acid anhydride (10 mL) in a 200-mL autoclave. Potassium peroxodisulfate (5.70 g, 21 mmol) was then suspended in the solution and the autoclave closed and flushed three times with methane (20 bar). Under stirring of the solution, the autoclave was pressurized with methane (20 atm) and heated to 80 °C. After 24 h the autoclave was cooled to –10 °C and the pressure slowly reduced. The cold, liquid reaction mixture was isolated and characterized by GC analysis.

Received: December 7, 2001 [Z18342]

- [1] Y. Fujiwara, T. Jintoku, Y. Uchida, *New J. Chem.* **1989**, *13*, 649–650.
- [2] R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560–564.
- [3] A. E. Shilov, A. A. Shteinman, *Kinet. Katal.* **1977**, *18*, 1129–1145.
- [4] H. Arakawa, M. Aresta, J. N. Armor, M. A. Barteau, E. J. Beckman, A. T. Bell, J. E. Bercaw, C. Creutz, E. Dinjus, D. A. Dixon, K. Domen, D. L. DuBois, J. Eckert, E. Fujita, D. H. Gibson, W. A. Goddard, D. W. Goodman, J. Keller, G. J. Kubas, H. H. Kung, J. E. Lyons, L. E. Manzer, T. J. Marks, K. Morokuma, K. M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W. M. H. Sachtler, L. D. Schmidt, A. Sen, G. A. Somorjai, P. C. Stair, B. R. Stults, W. Tumas, *Chem. Rev.* **2001**, *101*, 953–996.
- [5] H.-U. Wüstefeld, F. Schüth, W. C. Kaska, G. D. Stucky, GdCh Annual Conference, Würzburg, **2001**.
- [6] G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639.
- [7] S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem.* **1998**, *110*, 2298–2311; *Angew. Chem. Int. Ed.* **1998**, *37*, 2181–2192.
- [8] D. Wolf, *Angew. Chem.* **1998**, *110*, 3545–3547; *Angew. Chem. Int. Ed.* **1998**, *38*, 3351–3353.
- [9] R. H. Crabtree, *Chem. Rev.* **1995**, *95*, 987–1007.
- [10] R. H. Crabtree, *Chem. Rev.* **1995**, *95*, 2599.
- [11] K. Nakata, Y. Yamaoka, T. Miyata, Y. Taniguchi, K. Takaki, Y. Fujiwara, *J. Organomet. Chem.* **1994**, *473*, 329–334.
- [12] M. Kurioka, K. Nakata, T. Jintoku, Y. Taniguchi, K. Takaki, Y. Fujiwara, *Chem. Lett.* **1995**, 244.
- [13] Y. Taniguchi, T. Hayashida, H. Shibasaki, D. Piao, T. Kitamura, T. Yamaji, Y. Fujiwara, *Org. Lett.* **1999**, *1*, 557–559.
- [14] M. Asadullah, T. Kitamura, Y. Fujiwara, *Angew. Chem.* **2000**, *111*, 2609–2612; *Angew. Chem. Int. Ed.* **2000**, *39*, 2475–2478.
- [15] M. Lin, A. Sen, *Nature* **1994**, *368*, 613–615.
- [16] M. Lin, T. E. Hogan, A. Sen, *J. Am. Chem. Soc.* **1996**, *118*, 4574–4580.
- [17] J. Schwarz, V. P. W. Bohm, M. G. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773–1780.
- [18] T. Strassner, M. Muehlhofer, W. A. Herrmann, unpublished results, **2001**.
- [19] T. Strassner, unpublished results, **2001**.
- [20] A. L. Spek, PLUTON, Utrecht University, Utrecht, The Netherlands, **2001**.
- [21] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [22] A. D. Becke, *J. Chem. Phys.* **1992**, *97*, 9173–9177.
- [23] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [24] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [25] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631–2633; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490–2493.
- [26] T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem.* **1999**, *111*, 2573–2576; *Angew. Chem. Int. Ed.* **1999**, *38*, 2416–2419.
- [27] M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.
- [28] A. Fuerstner, O. R. Thiel, L. Ackermann, H.-J. Schanz, S. P. Nolan, *J. Org. Chem.* **2000**, *65*, 2204–2207.
- [29] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.
- [30] W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem.* **1993**, *105*, 1588–1609; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524–1544.
- [31] W. A. Herrmann, J. A. Kulpe, W. Konkol, H. Bahrmann, *J. Organomet. Chem.* **1990**, *389*, 85–101.
- [32] V. P. W. Bohm, T. Weskamp, C. W. K. Gstottmayr, W. A. Herrmann, *Angew. Chem.* **2000**, *112*, 1672–1674; *Angew. Chem. Int. Ed.* **2000**, *39*, 1602–1604.
- [33] W. A. Herrmann, M. Elison, J. Fischer, C. Koecher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374.
- [34] S. Caddick, F. G. N. Cloke, G. K. B. Clentsmith, P. B. Hitchcock, D. McKerrecher, L. R. Titcomb, M. R. V. Williams, *J. Organomet. Chem.* **2001**, *617–618*, 635–639.